All Organic Supercapacitors as Alternatives to Lithium Batteries

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14. ABSTRACT

The objectives of this work are to demonstrate at the laboratory scale a supercapacitor composed of conductive polymers as the electrodes that are separated by an environmentally benign electrolyte such as acetonitrile and tetraethyl ammonium triflate. The pertinent components of the capacitors must fit within the confines of a cylinder of 18 mm in diameter and 12.5 mm in height. Finally, the discharge properties of the capacitors must release a minimum of 0.2 J and maintain 0.02 W for a minimum of 10 s. These metrics are required for the potential application of these power sources in medium caliber munitions. In addition, each component of the supercapacitors must not pose a risk to the environment.

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Abbreviations

mA	milliamp
s	second
V	volt
J	Joules
W	Watts

Acknowledgements

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Executive Summary

Power supplies for the electronic fuses considered in the next generation of medium caliber munitions (20 – 60 mm) are primarily lithium-based chemical batteries. Lithium batteries are most commonly constructed from metallic lithium as the anode, thionyl chloride as the electrolyte, and a transition metal oxide or chalcogenide as the cathode. All three components are environmentally unacceptable and alternatives currently being used, such as sulfuryl chloride electrolytes, are equally harmful. Specifically, lithium metal reacts violently with water, causing burns and releasing hydrogen, which can ignite. Thionyl chloride and sulfuryl chloride are extremely caustic and decompose to yield hydrogen chloride, sulfur dioxide, and chlorine gas. The cathode materials often contain toxic cobalt. Repeated discharging of munitions containing lithium batteries will lead to long-term environmental problems and expensive clean up cost.

Alternatives to the lithium batteries must fit within the physical constraints of the medium caliber munitions, approximately a cylinder of 18 mm in diameter and 12.5 mm in height, and still provide comparable power and energy outputs. For the energy and power requirements, a supply of 4 V with a current drain of 20 – 200 mA for up to 10 s is required. For the proposed devices, a duel power supply will place two supercapacitors in series. With this arrangement, only 2 V are required for each capacitor and the energy capacity must be at least 0.2 J with an average power output of 0.02 W. In addition, the new power supply must be able to operate under the conditions of an extremely high linear acceleration (100+ KG) and spin rates (1000 – 1800 revolutions per second). Storage life times of more than 20 years and low cost are also desired.

Polymer supercapacitors fabricated from all-organic materials were evaluated as alternatives to the lithium battery power supplies. In these devices, electronically doped organic polymers replace the electrode materials of the lithium battery. Because the charging/discharging of the polymer materials involves ion migration, the polymer supercapacitor, sometimes referred to as a redox capacitor, can store charge after the potential has been removed. The organic nature of the polymers permits the use of environmentally benign electrolytes comprised of organic solvents and organic salts. With this approach, each component of the lithium battery alternative is substituted with a nontoxic and less corrosive replacement. Under this SERDP program, the discharge properties of poly(thiophene) based supercapacitors were investigated in combination with chemically innocuous electrolytes.

Polymer films were generated via the galvanostatic deposition of thiophene monomers on carbon paper or platinum mesh electrodes using acetonitrile electrolytes. Supercapacitors were constructed from two polythiophene films and an organic electrolyte under an inert atmosphere. After electrochemical charging, the discharge properties of the assembled capacitors were studied as a function of the type of polymer, electrolyte composition, and temperature. The performance of the polymer supercapacitors was found to vary considerable over a relatively small variation of the experimental parameters studied in this seed program. Energy and power outputs spanned an order of magnitude within the limited scope of this study. Most importantly,

the total energy and power output of 0.2 J and 0.02 W, the limits required by SERDP, were obtained.

Unlike previous studies on electrochemical capacitors, which focused on the cyclability of repeated charging/discharging steps, the present study centers on the initial 10 s discharge. The performance of the supercapacitors during this time frame is directly related to that expected during the trajectory of the medium caliber munitions. Earlier studies on polymer supercapacitors centered on developing rechargeable power supplies to supplement batteries. In these applications the total energy and power capacity of the supercapacitor are sacrificed in order to improve recyclablity. For the targeted applications of SERDP, recyclability is not an issue; rather total power and energy output must be maximized.

Objective

The objectives of this work are to demonstrate at the laboratory scale a supercapacitor composed of conductive polymers as the electrodes that are separated by an environmentally benign electrolyte such as acetonitrile and tetraethyl ammonium triflate. The pertinent components of the capacitors must fit within the confines of a cylinder of 18 mm in diameter and 12.5 mm in height. Finally, the discharge properties of the capacitors must release a minimum of 0.2 J and maintain 0.02 W for a minimum of 10 s. These metrics are required for the potential application of these power sources in medium caliber munitions. In addition, each component of the supercapacitors must not pose a risk to the environment.

Background

As the most electropositive metal, lithium has been used extensively in constructing high-energy batteries.[1] The highly negative reduction potential inherent to lithium (-3.05 V) and lightweight make for superior anodes surpassing most other metals in terms of energy density. In order to obtain batteries capable of providing significant currents (>200 mA) with voltages in excess of 3.5 V, electrolytes such as thionyl chloride $SOCl_2$ or sulfuryl chloride SO_2Cl_2 have been employed.[2] The combination of lithium metal and $SOCl_2$ or SO_2Cl_2 makes for toxic, corrosive, flammable, and potentially explosive batteries. Yet, replacing just the lithium anode with a more benign material will eliminate the requirement for the caustic electrolytes. Thus, our approach will focus on developing energy sources derived from all-organic supercapacitor.

Supercapacitors have been used commercially for sometime as power supplies to augment chemical batteries. Rechargeable batteries discharge at relatively low rates and, thus, have limited power supplies, Figure 1. When spikes in power are needed, a capacitor can supplement the primary energy source. The most common redox capacitor electrodes are comprised of toxic metals or costly nanocomposites.[3] Supercapacitors derived exclusively from low-cost organic polymers offer an inexpensive alternative. However, few studies have focused on applying these devices as a primary power source due to their relatively low energy densities, Figure 1. Since the energy required to power the electric fuses of medium caliber munitions are quite low and the high power demands are needed for only a short duration, the polymer supercapacitors are promising candidates for this specific and narrow application.

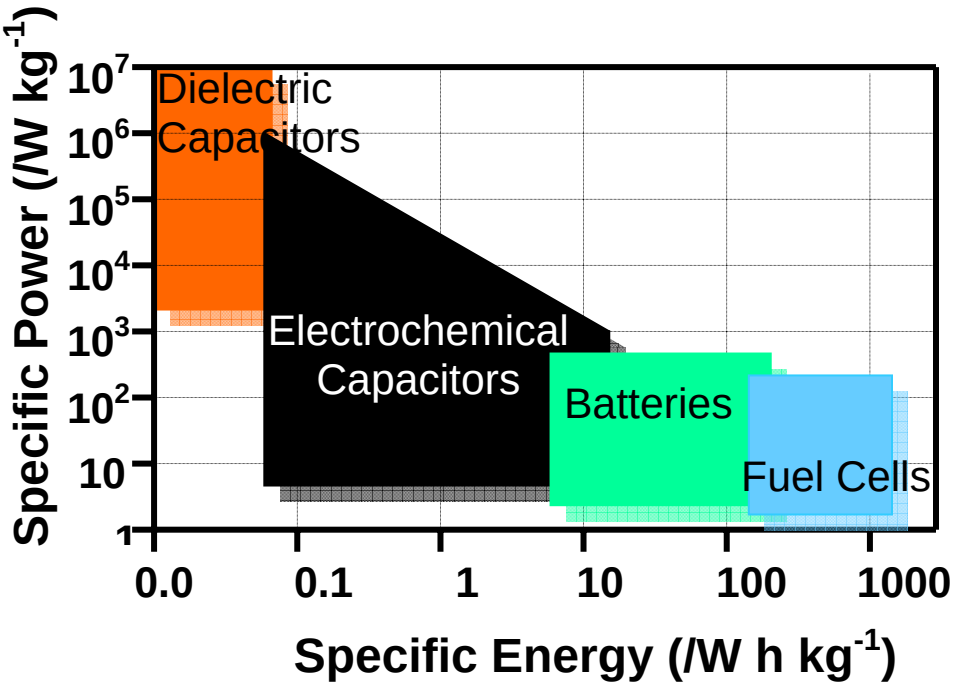


Figure 1. Ragone plot of common electrochemical devices.

The supercapacitors described in this proposal are especially convenient in that the polymer components are easily handled and processed and the devices are adaptable to existing methodologies for triggering including spin activation with out significant modifications.

Electroactive polymers such as polythiophene, polyacetylene, or polyaniline can be reduced, *n*-doped, or oxided, *p*-doped.[4] Reduction of the polymer raises the work function of the material and counter cations are incorporated into the polymer network during the process. Similarly, oxidizing an electroactive polymer lowers the work function of the material concomitant with anion intercalation. Electroactive polymers have been known for many years with applications in corrosion protection, sensors, LEDs, and non-linear optics.[5] As electrodes in an organic supercapacitor, the potential difference between the two polymer films provides the energy to drive electric currents and voltages.[6] Similarly, the energy difference between a lithium anode and a cobalt oxide cathode provide the potential energy in a lithium battery.

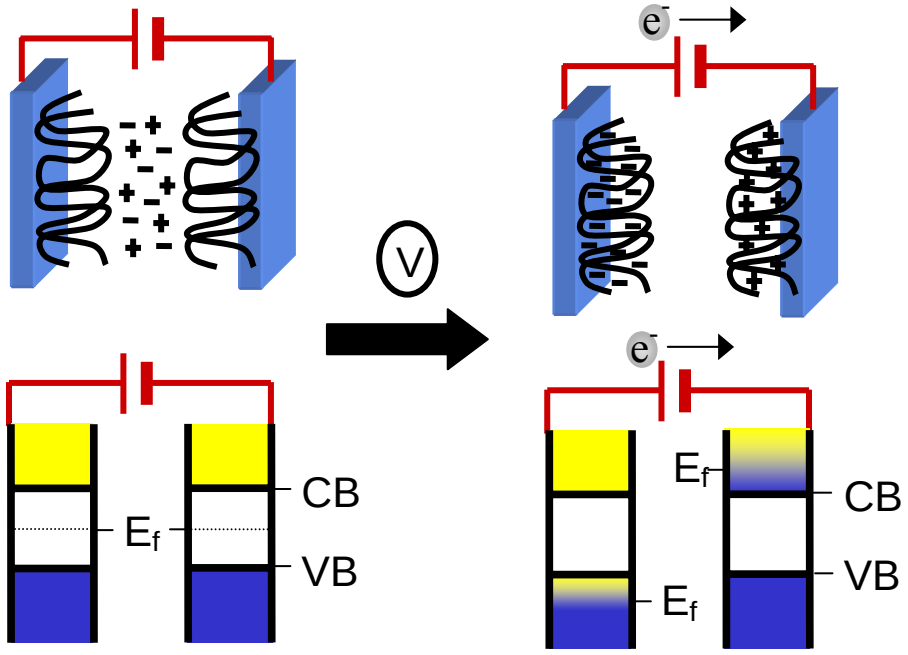


Figure 2. Prior to charging a polymer supercapacitor (top left), the polymer electrodes are neutral. After a potential is applied to charge the polymers (top right), charge compensating ions from the electrolyte migrate into the films. The energy diagram prior to charging has the Fermi level of the two polymer films equal (bottom left). After charging, the oxidized polymer has a lower Fermi energy and the reduced polymer has a higher Fermi level (bottom right).

As components of the supercapacitor, the *n*-doped and *p*-doped polymers must conduct both electrons and ions fast enough to deliver the desired currents. While the electronic conductivity of conjugated polymers has been studied quite extensively, very little is known about the ionic conductivity of these polymers.[7-10] Slow ionic diffusion

within the polymers will restrict the electrical discharge rates and limit the performance of the capacitor. Ghosh and coworkers have made polymer blends of polythiophene, a good electronic conductor, and polyethyleneoxide, a good ionic conductor, to improve the electrical discharge rate.[11] Unfortunately, this improvement occurred at a cost of capacity. To date, the ionic conductivity of conjugated polymers remains poorly understood. As a result many electrochemical properties of these polymers are difficult or impossible to predict because they depend strongly on the electrolyte. For example, films of poly(3-methylthiophene) are oxidized at 0.54 V vs. SCE with $LiPF_6$ electrolytes verses 0.66 V with $LiOSO_2CF_3$.[12]

By contrast, ionic conductivity in electrically insulating polymers such as polyethyleneoxide is well understood and many polymer electrolytes have been synthesized which take advantage of recent advances in understanding ionic motion in polymer salt complexes.[13] In many of these systems the segmental motion of the polymer backbone governs the mobility of the cations. To increase cationic motion, flexible polymers with low glass transition temperatures T_g are employed. For improved electrical conductivity in conjugated polymers, however, well-ordered and rigid structures are preferred.[9,10] These competing requirements will have to be balanced in order to construct supercapacitors with fast ionic and electronic conductivity. Still in other polymer electrolytes, ionic motion is relatively independent of the polymer motion.[14] In these systems the close proximity of low energy sites enables the cations to move through the material with only a minimal reorganization of the polymer.

Materials and Methods

Materials

Acetonitrile (CH_3CN) was purchased from Aldrich and dried over CaH_2 under a nitrogen atmosphere and distilled prior to use. Methylthiophene (Aldrich) was distilled under vacuum prior to use. Bithiophene, [1,3-bis(diphenylphosphino)propane]dichloronickel], 3-bromothiophene, and 4-fluorophenylmagnesium bromide (2.0 M in diethyl ether) were used as received from Aldrich. Carbon paper was obtained from E-Tek, New Jersey. Tetrabutylammonium tetrafluoroborate $[Bu_4N]BF_4$ and tetramethylammonium tetrafluoroborate $[Me_4N]BF_4$ were prepared by adding aqueous solutions of the tetraalkylammonium salt of hydrogen sulfate and ammonium tetrafluoroborate. The resulting precipitate was isolated by filtration and recrystallized from acetonitrile and ether.

Synthesis of 3-*p*-Fluorophenylthiophene

A 250 mL round bottom flask was equipped with a 25 mL constant pressure addition funnel, reflux condenser and nitrogen inlet/outlet. The glassware was dried in an oven at 140^{o}C for one hour and the assembly was allowed to cool under a positive nitrogen purge. After 30 minutes, the assembly was at ambient temperature, and the round bottom flask was charged with 60 ml dry ethyl ether, 26.6 mg [1,3-bis(diphenylphosphino)propane]dichloronickel (II)] ($NiCl_2$(dpp)) and 6.0 g (36.8 mmol) 3-bromothiophene. The round bottom flask was cooled to –10^{o}C in an ice/salt bath and after cooling the constant pressure addition funnel was charged with 18 mL 4-fluorophenylmagnesium bromide (2.0 M in diethyl ether). The 4-fluorophenylmagnesiumbromide was added drop-wise over 10 minutes, and the contents of the reaction flask were allowed to warm to ambient temperature. A solid percipitate was present in the flask, which was filtered and the paste dried in a vacuum dessicator (0.05Torr, 25^{o}C) to constant weight. The crude off-white powder was recrystallized from methanol/water (1:4 v/v) mixture to give an off-white powder. The off-white powder was further purified via sublimation (0.05 Torr, 100^{o}C). The powder was dried in a vacuum dessicator (0.05Torr, 25^{o}C) to constant weight to give a fine white powder in 1.39 g (21% yield). ^{1}H NMR and ^{13}C NMR showed product obtained, GC/MS purity = 99.88%.

Polymer Electrodes

In a nitrogen-purged glove box, carbon paper or platinum mesh electrodes were immersed in 0.1 M solutions of the thiophene monomer in acetonitrile that was 0.1 M in $[Bu_4N]BF_4$. The poly(thiophenes) were deposited galvanostatically with an oxidizing current density of about 10 mA/cm^2. Subsequently, the polymer films on the carbon electrodes were washed with clean acetonitrile and allowed to dry under nitrogen. The polymer films were investigated electrochemically with cyclic voltammetry with 1 M $[Bu_4N]BF_4$ acetonitrile solutions, a platinum counter electrode and a Ag/Ag^+ reference electrode. Two electrode cells composed of a polymer working and polymer counter

electrodes were used to construct the all-organic supercapacitors. Each capacitor was charged with a 3.5-4.5 V potential for 3000 s and allowed to discharge at a set current. The resulting potential was measured over the initial 10 s of the discharge. All electrochemical measurements were performed with a PAR 273A potentiostat/galvanostat. The reported discharge potentials are not corrected for solution resistance.

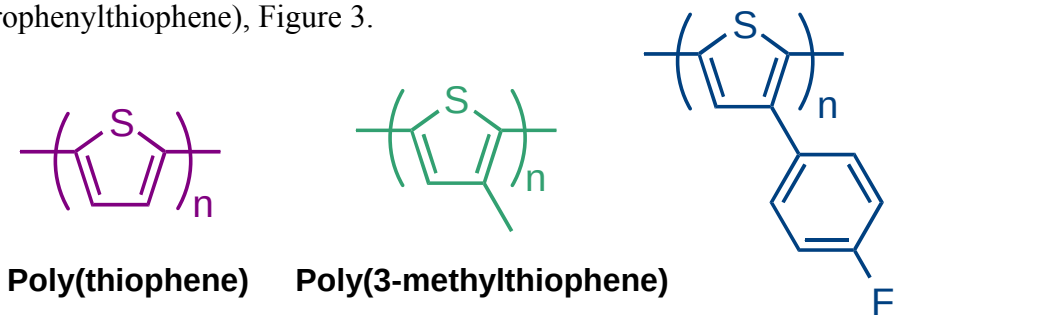
Results and Accomplishments

Monomer Synthesis

Efforts to synthesize the monomer *p*-fluorophenylthiophene using published procedures resulted in a product containing 4,4'-difluorophenyl which could not be removed by repeated recrystallizations.[15] Although, the 4,4'-difluorophenyl impurity would likely not affect the polymerization of the *p*-fluorophenylthiophene, the diphenyl could compromise the performance of supercapacitors containing the resulting poly(3-*p*-fluorophenylthiophene) electrodes. An alternative route to *p*-fluorophenylthiophene was found by simply replacing the use of tetrahydrofuran with diethylether. This procedure resulted in spectroscopically pure material with slightly lower yields. This new synthetic procedure was used for the production of the *p*-fluorophenylthiophene used in this work.

Polymer films

For this seed program three types of polymers were investigated as electrodes in the supercapacitor: poly(thiophene), poly(3-methylthiophene), and poly(3-*p*-fluorophenylthiophene), Figure 3.



Poly(thiophene) **Poly(3-methylthiophene)**

Poly(3-*p*-fluorophenylthiophene)

Figure 3. Structures of poly(thiophene) (purple), poly(3-methylthiophene) (green) and poly(3-*p*-fluorophenylthiophene).

Electrochemical polymerization of thiophene monomers occurs at anodic potentials. Polymer films can be grown potentiostatically or galvanostatically. Cycling the potential of a platinum electrode in a solution of thiophene monomer results in increasing current with each subsequent sweep. This increased current is a result of the formation of the parent polymer as a film on the working electrode, Figure 4. Alternatively, polymer films can be grown galvanostatically with anodic currents. For the present work, this technique was preferred because it yielded thicker polymer films in shorter deposition times. However, the deposition of the polythiophenes was not uniform over the surface of the carbon paper.

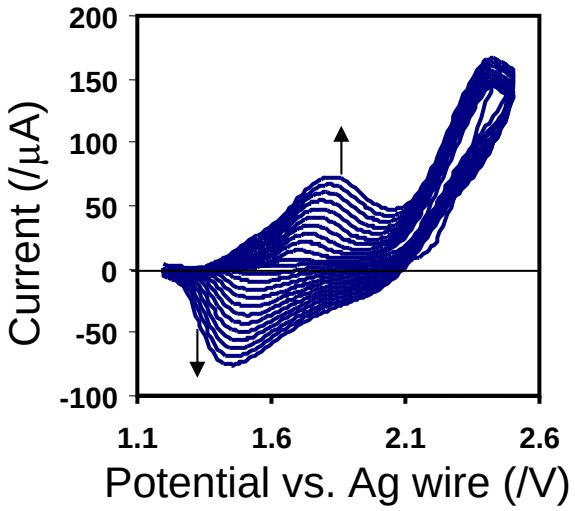


Figure 4. Cyclic voltammogram of a platinum disk electrode in a 0.1 M solution of FT in acetononitrile, 0.1 M in $[Bu_4N]BF_4$. The arrows indicate the direction of increased current with each subsequent sweep.

Deposition of the polymer films occurs preferentially at the edges and corners of the working electrode that are in closet proximity to the counter electrode. Despite this lack of film uniformity, repeated experiments with polymers derived from the same monomer produced similar results and total capacity and power outputs were found to vary by only 10 % from one device to the next.

The electrochemical doping of each polymer is dependent on the monomer type and electrolytes. Cyclic voltammetry on the polymer films in clean electrolytes reveals both the oxidation and reduction potentials of the film, Figure 5. In assembling a supercapacitor from two polymers, the upper limit of the output voltage is determined by the difference in the reduction potential of the n-type polymer and the oxidation potential of the p-type polymer. Thus, a supercapacitor composed of two of these polymer electrodes can be expected to provide upwards of 2.5 V. This is significantly less than the 3.5 – 4 V obtained with lithium batteries. To achieve these higher voltages, two polymer supercapacitors will be paired in series, Figure 6. The total potential difference will be the sum of the two devices. With this configuration, the total current passing through the circuit will be limited by the supercapacitor with the lowest current or capacity. Thus, *each supercapacitor element must maintain the 20 mA discharge at 2V for 10 sec*. These quantities are required to meet the energy and power supply metrics set by SERDP.

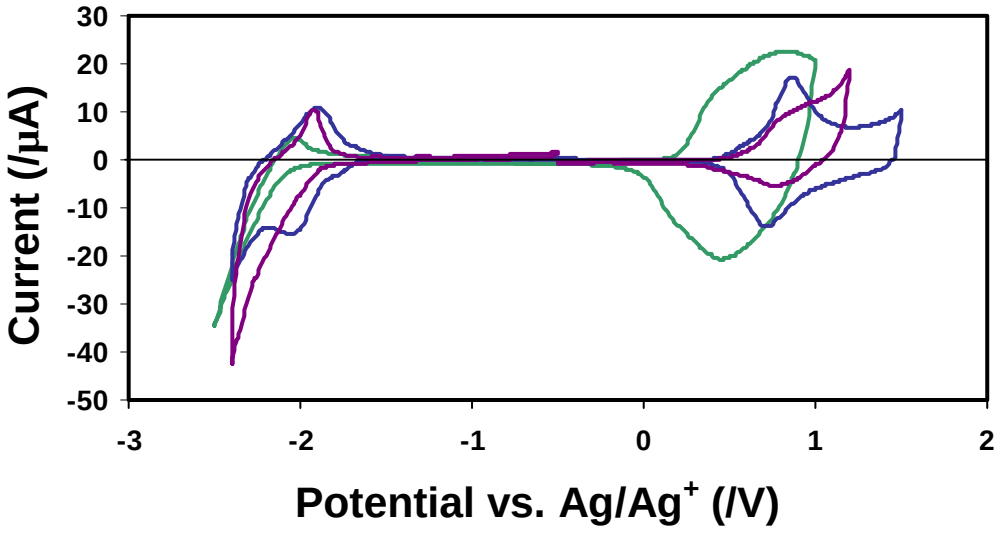


Figure 4. Cyclic voltammograms of poly(thiophene) (purple), poly(3-methylthiophene) (green) and poly(3-*p*-fluorophenylthiophene) on platinum disk electrodes with 0.1 M $[Bu_4N]BF_4$ in CH_3CN electrolyte.

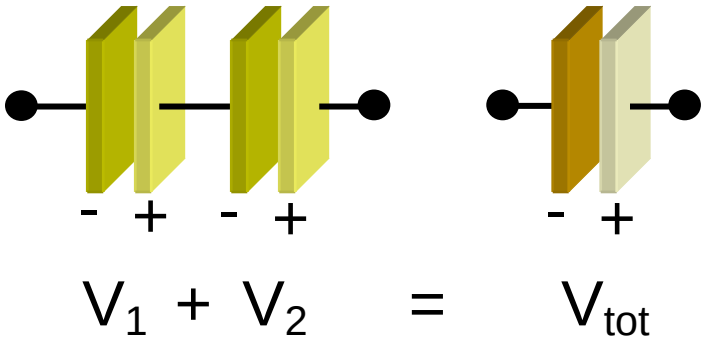


Figure 5. The total voltage, V_{tot}, of two supercapacitors in series is a sum of the two individual capacitors, V_1 and V_2. As long as V_1 and V_2 are larger than 2 V, then the voltage difference across the pair in series will be greater than 4 V, the SERDP requirement.

Polymer Supercapacitors

The electrochemical charging of the polymer supercapacitor is accomplished by biasing one-polymer electrode verses the other in a two-electrode configuration. The direction of the bias determines which film is oxidized (p-doped) or reduced (n-doped). In the present work, polymer supercapacitors were charged at 4 V for 300 – 3000 sec. The charging current rapidly decreases over the first two minutes and eventually plateaus, Figure 6A. The amount of charge/polymer repeat-unit can be calculated by integrating

the current and measuring the mass of the polymer film. Values of 5 – 10 electrons/repeat unit were obtained under the experimental conditions employed. These values are consistent with those obtained with other electroactive polymers.[15] At short circuit (0 V) the discharge current of the polymer supercapacitors drops rapidly and within 30 seconds over 80 % of the total capacity is discharged, Figure 6B.

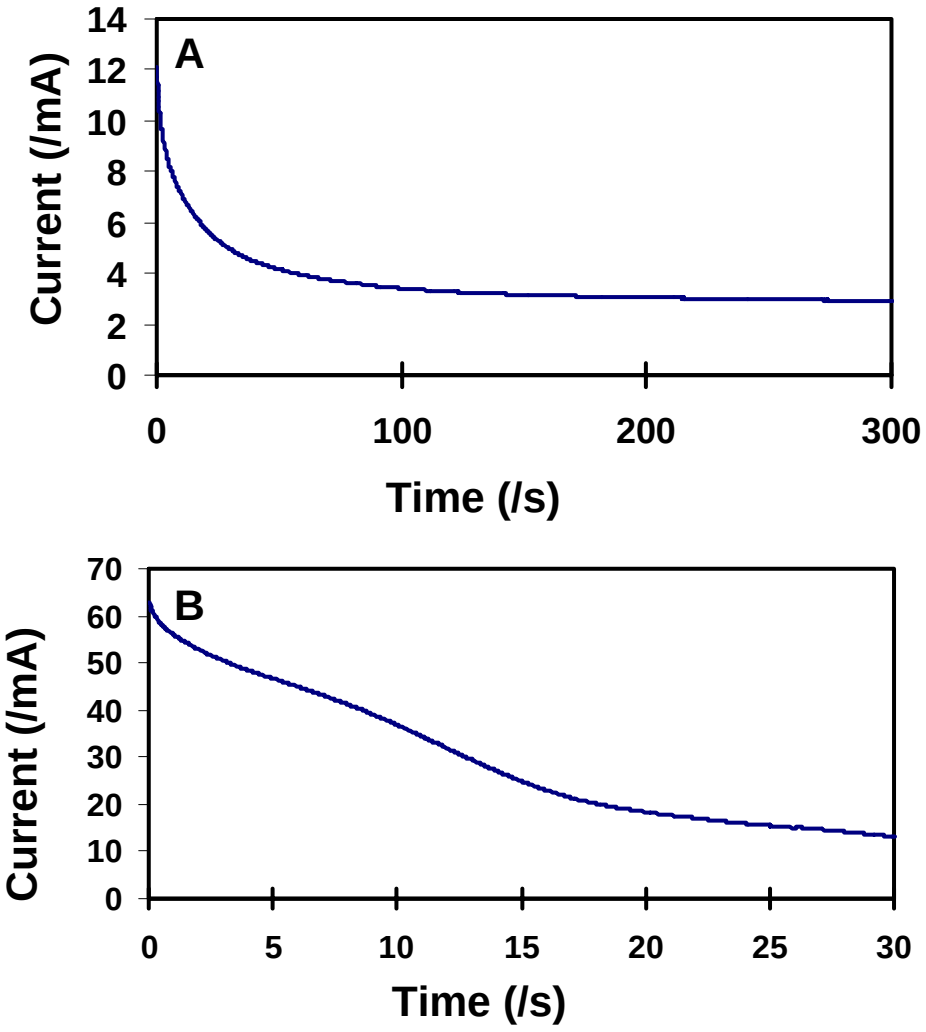


Figure 6. (A) Charging current for a poly(3-methylthiophene)/0.1 M $[Me_4N]BF_4$ in CH_3CN/poly(3-methylthiophene) supercapacitor. Total charge indicates approximately 1 electron/8 repeat units in the polymer. Higher capacity densities are possible with longer charging times or higher charging potentials. (B) Short circuit current of a poly(3-methylthiophene)/0.1 M $[Me_4N]BF_4$ in CH_3CN/poly(3-methylthiophene) supercapacitor. Electrode areas are 1 cm^2 each.

The discharge properties of the polymer supercapacitors are a function of the types of polymers used in the anode and cathode, electrolyte, charging time, charging potential, and temperature. Initial work centered on the poly(3-methylthiophene)/0.1 M $[Me_4N]BF_4$ in CH_3CN/poly(3-methylthiophene) supercapacitor since this combination has been studied in the past for potential applications as rechargeable auxiliary power supplies.[16] Subsequent studies focused on variations in the cathode and anode polymers and the type of electrolyte. In order to compare one device to the next, similar charging potentials and times were employed, 4.5 V and 3000 s respectively. For the SERDP requirements, the discharge potentials were measured at current densities of 1, 5, and 20 mA/cm^2 over a ten second period. Under these conditions, a polymer supercapacitor must maintain a minimum discharge voltage of 2 V at the 20 mA/cm^2 rate to meet the SERDP metrics. These values correlate to a total energy output of 0.2 J and a power output of 0.02 W for the 10 s duration.

Supercapacitors with poly(3-methylthiophene) cathodes were investigated with 0.1 M $[Bu_4N]BF_4$ in CH_3CN and various polymer anodes. The charging and discharging protocols were uniform for the different devices. Discharge potentials vary over a wide range despite the small variation in the anode materials, Figure 8. At low current densities (1 or 5 mA/cm^2) the discharge potentials were in excess of 2 V for the entire 10 s duration for each type of polymer cathode. However, at discharge currents of 20 mA/cm^2 the discharge potentials fall well below 2 V. Within six seconds the discharge potentials for the poly(3-methylthiophene) and poly(3-*p*-fluorophenylthiophene) devices become negative. Only the poly(thiophene) cathode maintains a positive discharge potential for 10 s.

Integrating the discharge potentials yields the total energy output. These values are shown in the bottom left corner of the discharge plots in Figure 8. Simple changes in the anode material yields an order of magnitude variation in the energy storage capability of the supercapacitors. Yet, none of the polymer anodes produces the requisite 0.2 J. However, these results do demonstrate that minor changes in the polymer materials used to construct the capacitors can have substantial effects on the device performance. Furthermore, with the appropriate side-groups, functionalized polythiophene materials may provide significantly higher energy capacity than currently observed.

The effect of the electrolyte composition was briefly investigated. In these studies, the tetrabutylammonium cation was replaced with the smaller tetramethylammonium. The discharge potentials for the two best performing supercapacitor polymer combinations are shown in Figure 9. Discharge potentials at low current densities are similar to those observed for the tetrabutylammonium electrolytes. At these low currents and capacity discharges, the material compositions of the polymer and electrolyte have negligible affects. However, at the high discharge currents which are more relevant to military applications, a seven fold increase in the energy capacity for the poly(3-methylthiophene) anode and a 50% increase for the poly(thiophene) anode are observed with the tetramethylammonium electrolyte. Clearly, the size of the counter ion and the nature of the polymer/cation interaction are important in determining the rates at which the supercapacitors release all of their energy.

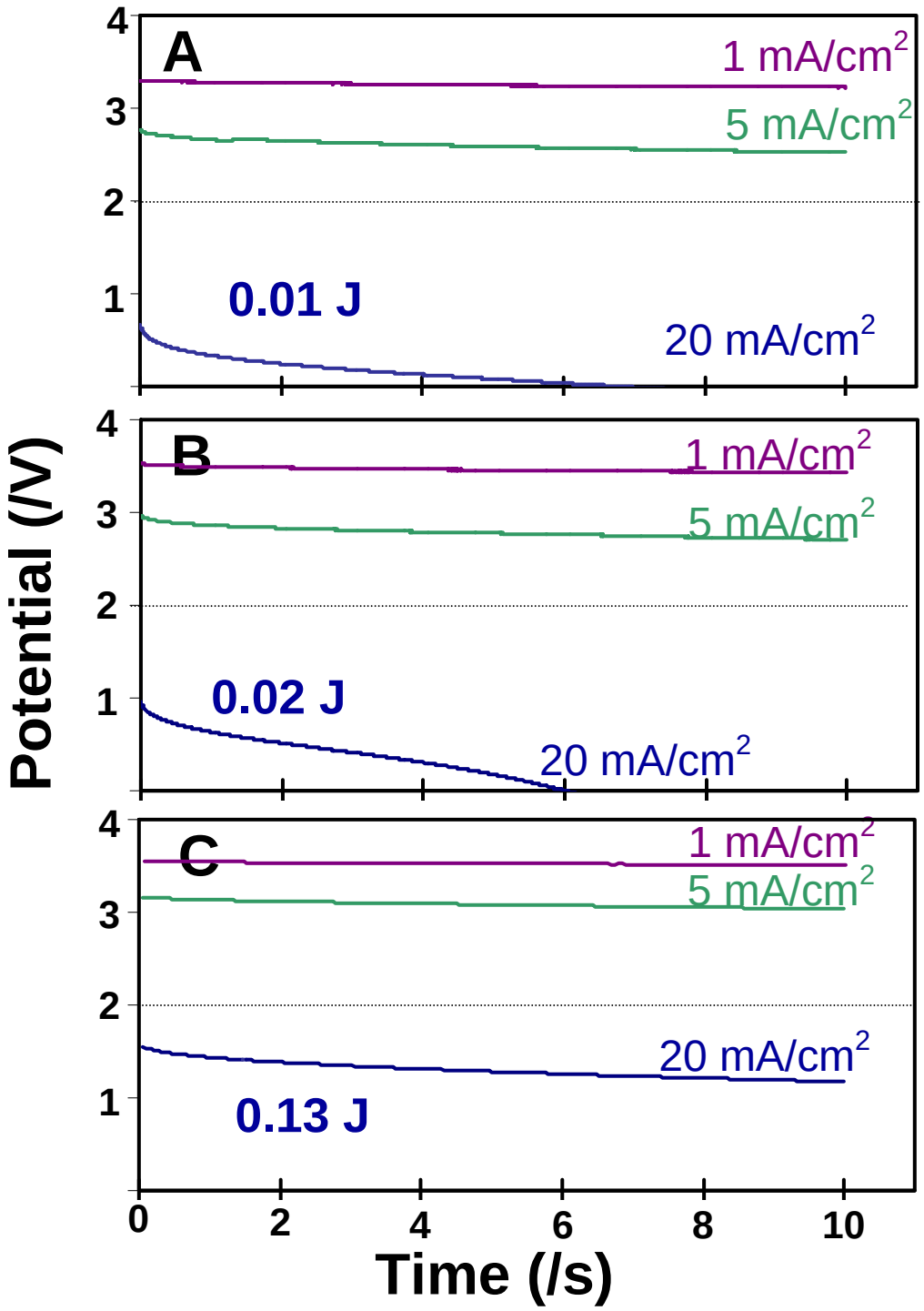


Figure 8. Discharge potentials for polymer supercapacitors composed of (A) poly(3-*p*-fluorophenylthiophene) (top), (B) poly(3-methylthiophene) (middle), and (C) poly(thiophene) (bottom) anodes with poly(3-methylthiophene) cathodes and 0.1 M $[Bu_4N]BF_4$ in CH_3CN electrolytes.

Presumably the smaller tetramethylammonium cation can migrate through the polymer film more easily than the larger tetrabutylammonium. Films with larger surface area and/or mass may provide supercapacitors with a higher total capacitance and, thus, be less dependent on the polymer materials or electrolyte composition.

Most significantly, the higher capacity exhibited with the tetramethylammonium electrolytes are on the order of the SERDP requirements. In fact, the poly(thiophene)/0.1 M $[Me_4N]BF_4$ in CH_3CN/poly(3-methylthiophene) device has a total energy release of 0.21 J which surpasses the 0.2 J threshold. The power output of this device lags slightly below the required 0.02 W in the last second of the 10 s discharge.

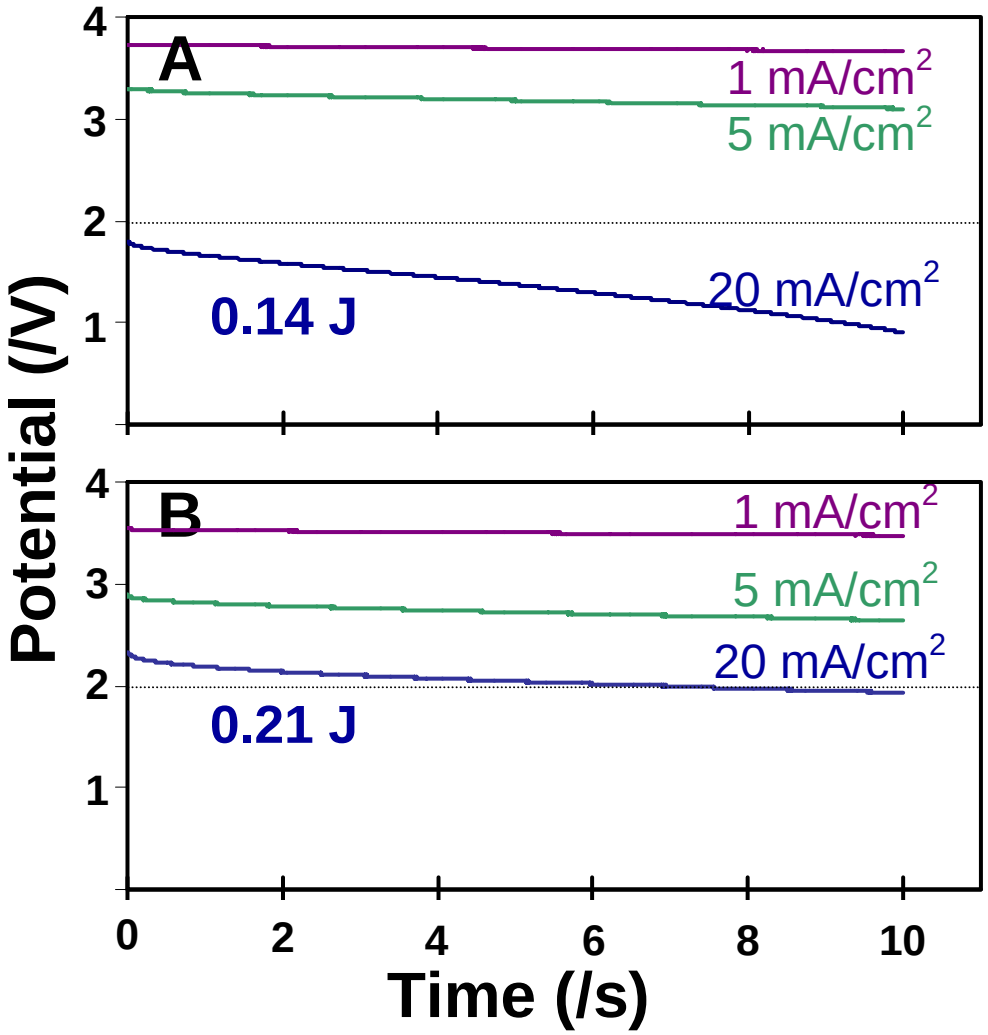


Figure 9. Discharge potentials for polymer supercapacitors composed of (A) poly(3-methylthiophene) (top), and (C) poly(thiophene) (bottom) anodes with poly(3-methylthiophene) cathodes and 0.1 M $[Me_4N]BF_4$ in CH_3CN electrolytes.

The best performing anode/electrolyte combinations, poly(thiophene)/0.1 M $[Me_4N]BF_4$ in CH_3CN, were investigated with different cathode materials, Figure 10. Varying the cathode material from poly(thiophene) to poly(3-methylthiophene) or poly(3-*p*-fluorophenylthiophene) result in a net decrease in performance. Both the total energy released during the first 10 s and the average power output are significantly lower than devices employing the poly(thiophene) cathode at 20 mA/cm^2 discharge rates, compare Figure 9B and 10B. As the cathode material is discharged, counter anions are expelled from the polymer matrix. More mobile anions such as smaller chloride ions or weaker coordinating ions such as triflate, $^-OSO_2CF_3$, may provide a lower resistance and higher discharge potentials.

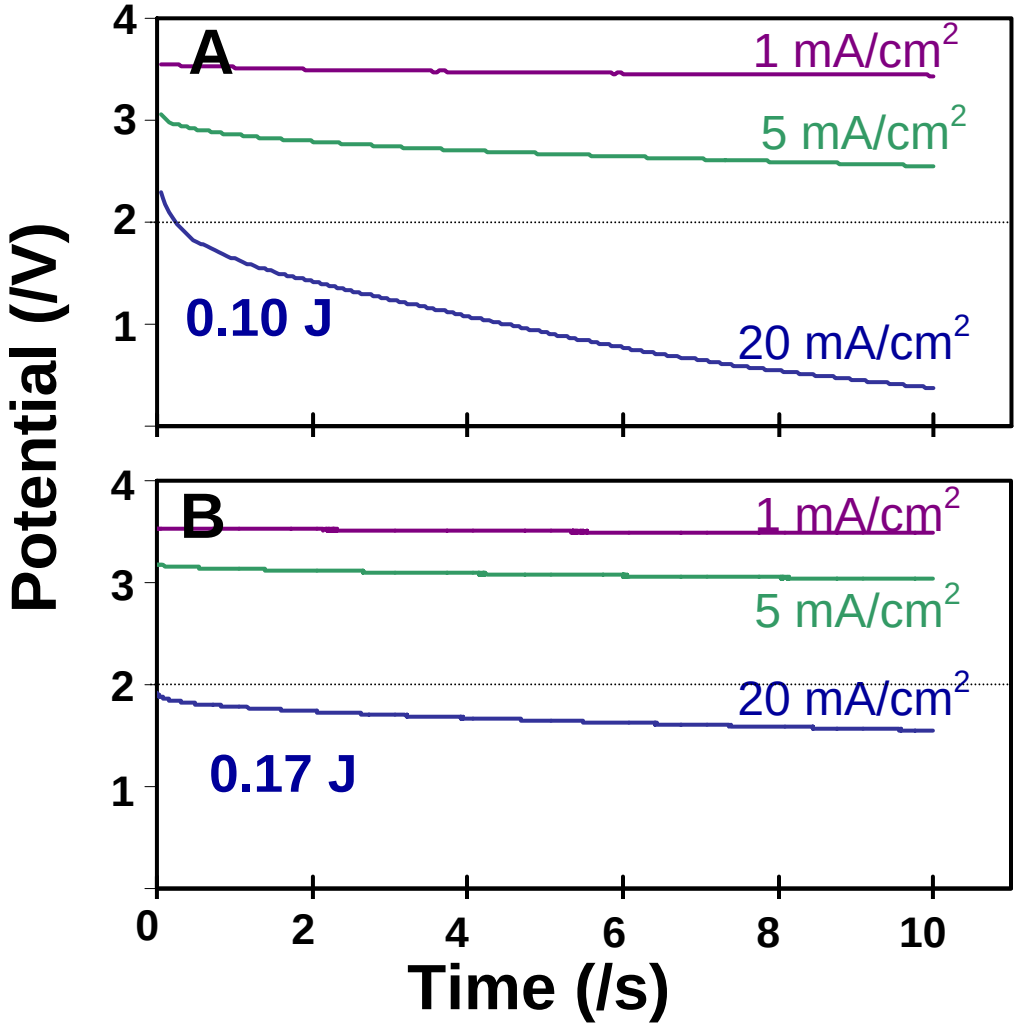


Figure 10. Discharge potentials for (A) poly(3-*p*-fluorophenylthiophene) (top) and (B) poly(thiophene) cathodes coupled with poly(thiophene) anodes and 0.1 M $[Me_4N]BF_4$ in CH_3CN electrolytes.

The importance of the electrolyte in determining the electrical performance of the polymer supercapacitors cannot be overstated. In addition to providing counter ions in the doped polymer matrices, the electrolyte reduces the overall cell resistance. With the electrode geometry and organic electrolyte, cell resistances were on the order of 20 Ω. A discharge current of 20 mA yields a potential drop of 0.4 V. As stated in the experimental section, all of the reported data is not corrected for solution resistance. The electrode separations used in the experimental set up were on the order of 1 – 2 cm. When configured for applications in medium caliber munitions, this distance would shrink to approximately 1 mm. The cell resistance in this more compact configuration would reduce the potential drop across the cell by an order of magnitude. Thus, the discharge potentials for these supercapacitors would be higher by approximately 0.35 V.

Finally, the temperature dependence on the discharge properties was investigated. Data was collected at 63˚C, 24˚C, and -23˚C for the best performing anode/electrolyte/cathode combination reported, Figure 11. Comparable discharge potentials are observed for the room temperature and the elevated temperature measurements. However, at low temperatures a discharge current of only 5 mA/cm^2 could be achieved. At these temperatures the $[Me_4N]BF_4$ started to precipitate from solution. Consequently, the solution resistance increased dramatically increasing the cell over potential. Although the low temperature observations are disappointing, they can likely be overcome with more soluble/stable electrolytes such as molten salts that remain highly conductive at depressed temperatures.

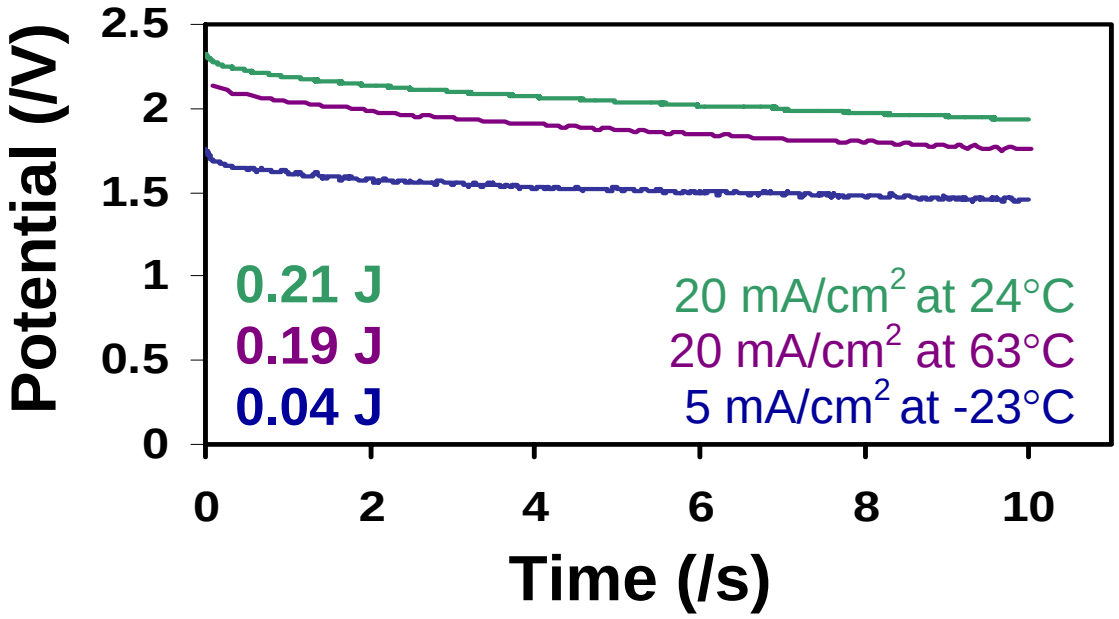


Figure 11. Discharge potentials for poly(3-methylthiophene)/0.1 M $[Me_4N]BF_4$ in CH_3CN/ poly(thiophene) with cathodes and electrolytes at various temperatures.

The carbon paper electrodes can be substituted with platinum mesh. In these devices the polymer films are deposited on the metal and supercapacitors can be assembled from two polymer-coated platinum electrodes. The surface areas of these electrodes are poorly defined and a quantitative comparison is difficult. However, similar capacitances and discharge properties to devices constructed from carbon paper can be obtained with polymer films deposited on platinum mesh of similar areas. In addition the platinum electrodes tend to be more stable at higher potentials than the carbon analogs. In munitions applications the more robust platinum may be preferred.

Once charged, the supercapacitors are vulnerable to losing the stored energy. Specifically, impurities in the electrolyte can lead to electrically conductive electrolytes and, in effect, short the anode and cathode. Similar processes shorten the shelf life of chemical batteries. These impurities can contribute to a loss in the supercapacitor performance and shorten the lifetime of the capacitor. In the present devices, the charging and discharging experiments were conducted in the same electrolyte solution. Upon charging of the supercapacitor, short chain oligomers dissolve from the anode as evident by a discoloration of the electrolyte. These oligomers likely serve as redox active impurities that deteriorate the capacitance of the films. Under the short time frame of the laboratory experiments, these devices are able to provide the necessary charge at an acceptable rate. However, the overall capacitance deteriorates with time. The shelf life of these supercapacitors can span hours depending on level of impurities in the electrolyte. To increase the lifetimes of the supercapacitors, the polymer electrodes must be thoroughly rinsed in clean electrolyte after deposition. This process removes some of the short chain molecules. Further cleaning of the polymer films after cathodic charging results in the additional removal of fragments. Under these conditions the lifetime of the charged supercapacitor is greatly increased to at least days. Due to the limited scope of this seed program, the maximum lifetime of the supercapacitors was not determined. However, the redox properties of the supercapacitors greatly resemble that of chemical batteries. As such, protecting the devices from impurities generated during the production process or contaminants such as oxygen will greatly extend their shelf life. Under the most stringent conditions, the shelf life for the supercapacitors should be comparable to that of chemical batteries.

Conclusions

The organic polymer-based supercapacitors studied in this SERDP seed project are viable alternatives to lithium batteries in medium caliber munitions. To replace the high-energy capacity of lithium metal, two capacitors in series are needed. This requirement does not prohibitively reduce the size constraints on the supercapacitors. In fact, all of the devices described in this study can be assembled in volumes that are only a fraction of that allotted by the medium caliber munitions. A series of four capacitors as described can easily fit within the space requirements, thereby further increasing the energy supply. However, only two polymer capacitors were needed to obtain the 4 V requirement set by SERDP.

As described in the results section, single supercapacitors yield voltages of 2 V for 90 % of the 10 s discharge and a total energy output of 0.21 J. The fact that the energy metrics were reached with the limited scope of materials and electrolytes investigated in this one-year program suggests that even greater capacities are possible with a more detailed study of different composition. For example poly(acetylene) films have significantly larger electrochemical windows suggesting that larger voltages would be possible with these materials. In fact, poly(acetylene) has been explored as a cathode material for lithium batteries.[4] With additional focus on alternative polymer materials and electrolytes, both the energy and power requirements can easily be improved. The majority of work in this area has centered on developing recyclable capacitors as auxiliary power supplies for battery operated devices. To our knowledge, this work is the first to adapt supercapacitors as the primary energy source.

The long-term physical and chemical stability of the polymer supercapacitors have not been explored in great detail. The supercapacitors studied in this work primarily employed carbon paper as the support electrode. However, similar results were obtained with the more robust platinum mesh electrodes. These metal alternatives can be used if the carbon paper proves too fragile at the high spin rates. The platinum-plated mesh will likely have a lower the cost than the carbon paper. More important is the chemical stability of the polymer supercapacitors. As stated previously, this study is the first to adapt the polymer supercapacitors for primary energy storage. Given the chemical similarity of these devices to chemical batteries, there is no reason that the shelf life of the supercapacitors will not be comparable to conventional batteries. In the present work, the chemical stability of the polymer supercapacitors was found to depend largely on the purity of the electrolyte, as is the case for chemical batteries. Within spin-activated munitions, the electrolyte and electrodes are separated during storage and combined only when fired. In this arrangement, the charged polymer films would be indefinitely stable. However, a more in depth study is needed in which a charged polymer capacitor is separated from the electrolyte, reimmersed, and discharged.

In the current manifestation, the polymer supercapacitors are limited in their operational temperature range. This restriction is likely due to the instability of the acetonitrile electrolyte at low temperatures. The organic salts precipitate out as the temperature is decreased, thereby, increasing the solution resistance and compromising the performance of the capacitor. Viable alternatives to the tetraalkyl ammonium slats include molten salts, which are ionic liquids. These salts can be dissolved in organic

solvents without risk of precipitation as long as the temperature remains above their freezing point. With these electrolytes, the operational temperature of the supercapacitors should be extended to well below -50˚C.

Since each component of the polymer supercapacitor affects its discharge properties, care must be taken to identify the combination of anode, cathode, and electrolyte to yield the maximum capacitance and stability under a variety of conditions. For example, the optimal anode material with one electrolyte may not give the highest capacitance with another electrolyte. This interdependence may complicate identifying the ideal composition for the supercapacitors but it also increases the likelihood of producing even better performing devices. In addition, the data within this report sets a lower limit on the supercapacitor performance, which is already adequate for current munitions applications. Within this framework, the polymer supercapacitors promise to fulfill the energy and power needs of the medium caliber munitions of the future with environmentally friendly materials.

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